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METHOD FOR PRODUCTION OF REACTIVE MATERIAL TYPES AND METHOD FOR MODIFICATION OF SURFACE OF A SOLID MATERIAL

[Verfahren zur Herstellung reakionsfähiger Materíalformen und Verfahren zur Modifizierung einer Oberfläche eines festen Materials]

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Description

The present invention relates to a method for production of highly reactive material types or products using a UV laser beam and also it relates to a method for modification of a surface of a solid material using the material type so produced and/or using products.

At present, comprehensive basic studies and applications of processing a surface of an organic material, typically a polymer material, have been undertaken using an oscillating, pulsed excimer laser beam of high intensity in an ultraviolet range for development of a new method for exact treatment and processing of a surface of an organic material. The Japanese patent JP-A-63177414 discloses a laser ablation method with which a target which is frozen at a low temperature and made from a metal or a semiconductor raw material is irradiated with a laser beam in order to produce a plasma out of the raw material, and the plasma can be deposited on a solid substrate and a highly pure layer is obtained from a semiconductor, a metal or a dielectric substance. JP-B-7-5773 discloses a method for activation of a surface of a shaped material made from fluorine-contained polymer by means of irradiation with a UV laser beam in the presence of a hydrazine compound. In this method, hydrazine molecules are disintegrated by the laser beam in a vapor phase, and the disintegrated molecules are again brought into a reaction with the surface of the shaped material. A disadvantage of this method is that the disintegration takes place in the vapor phase by which it is difficult to control the compound or to control the state of disintegrated materials.

The task of this invention is to avoid the disadvantages mentioned above.

This problem is solved according to the invention in that a method is developed for production of reactive material types which is characterized in that a solid layer formed on the substrate is irradiated with an ultraviolet laser beam having a wavelength of 400 nm or shorter, whereby the solid layer is formed from a mixture of a matrix material with a photoreactive substance.

According to another aspect, the present invention develops a method for modification of a surface of a solid material which is characterized in that the surface is brought into contact with the reactive material types that were produced according to the above method.

This invention is described in detail with reference to the attached drawings.

Figure 1 is an emission spectrum of vaporized products that were emitted by a solid material which was irradiated with a UV laser beam.

Figure 2 is an X-ray- photoelectron spectrum of a polyethylene terephthalate layer before irradiation with the vaporized products.

Figure 3 is an X-ray photoelectron spectrum of a polyethylene terephthalate layer after irradiation with the vaporized products.

A solid layer which is formed on a substrate is irradiated with a UV laser beam according to the invention. The solid layer was produced from a mixture of a matrix material with a photoreactive substance. Any material can be used as the photoreactive substance as long as it shows absorption in the UV range. The photoreactive substance is preferably a compound which can be disintegrated by irradiation with a UV beam, such as an azide compound, an azo compound, a carbonyl compound, an acid anhydride, a hydrazine or an organic halogen compound. The photoreactive substance can have the state of a solid, a fluid or a gas at room temperature; however, it must exist in the solid state under the conditions under which the method of this invention is implemented.

The matrix material is a substance which does not considerably show absorption in the UV range. Examples of matrix material comprise noble gases, a nitrogen gas, carbon dioxide, a fluorinated alkane, alkane, ether and alcohols. It is desirable that the matrix material cannot be easily disintegrated by irradiation with UV beam. The matrix material can be a solid, a fluid or a gas at room temperature; however, it must exist in the solid state under the conditions under which the method of this invention is

implemented. The quantity of the photoreactive substance in the solid layer is generally 50 mol% or less, preferably 0.01-1 mol-% with respect to the matrix material.

The solid layer can have a single-layer structure or a multi-layer structure. The solid layer can be a single layer made from a matrix material in which only one type of photoreactive substance is dispersed. If desired, two or more photoreactive substances can be contained in a single layer made from matrix material. Further, two or more photoreactive substances can be incorporated correspondingly in two or more layers made from matrix material.

The substrate can be manufactured from any arbitrary material as long as the material does not react to the matrix material; it is desirable that it be a thermoconductive material. A metal such as silver, a metal oxide such as sapphire, an inorganic crystal such as cesium iodide, can be preferably used as the substrate. The substrate is retained at a temperature which allows the matrix to exist on it as a solid. For example, the substrate is cooled to 200 K or lower, preferably not higher than the temperature of liquid nitrogen if an alkane is used as the substrate. In case of a noble gas matrix, the substrate is kept at its Debye temperature, typically at 20 K or lower.

The laser used for the purpose of this invention is selected suitably according to the photoreactive substance such that the oscillating laser beam is absorbed by the photoreactive substance. The usage of an excimer laser such as ArF excimer laser (wavelength 193 nm), a KrF excimer laser (wavelength 248 nm), a XeCl excimer laser (wavelength 308 nm) or a XeF excimer laser (wavelength 351 nm) is preferred since the beam diameter is large. A laser beam which is obtained by modulation of a Nd+ YAG laser, a dye laser, a Kr ion laser, an Ar-ion laser or a Cu-vapor laser with a non-linear optical element in order to achieve a wavelength of 400 nm or shorter, can be used. The flow of the laser varies with the type of photoreactive substance. It is preferred that the laser have an intensity of about

1 mJ/cm^2/ pulse or more, preferably 5 mJ/cm^2/ pulse or more, for a pulse width in the nano second range.

The solid layer which is made from a mixture of the matrix material with the photoreactive substance can be obtained by bringing into contact the mixture with a substrate; this substrate is cooled to a temperature that is sufficient for solidification of matrix material. If the matrix material is for example, a fluid at room temperature, then a solution of the photoreactive substance is obtained; this solution is dissolved in the matrix material, and it is applied on the surface of the substrate by spraying or pouring. Said substrate is held at a temperature lower than the solidification point of the matrix material by which a solid layer is obtained from the mixture on the substrate surface. If the matrix material is a gas at room temperature, then a mixture is obtained which is the gaseous matrix material in which a gaseous substance or a mist from a photoreactive substance is dispersed; it is inflated or radiated on the surface of the substrate whereby the substrate is held at a low temperature sufficient to allow the matrix material to solidify on account of which a solid layer is obtained from the mixture on the substrate surface.

The solid layer is irradiated with the UV laser beam such that the photoreactive substance is converted into a reactive type of material which is emitted by the solid layer. In this way, the solid layer is ablated. The reactive material types are high reactive photo-disintegration products in the form of ions, radicals, etc.

The surface can be modified or activated by bringing in contact the reactive material types produced according to the above method with a surface of a solid material. The surface modification takes place by reaction of molecules of the surface of solid material with the reactive material types. If the reactive material types contain, for example, oxygen atoms or nitrogen atoms, then the hydrophilicity of the surface of the solid material is improved by the reaction with them. If the reactive material types contain

fluorine atoms, then, the hydrophobic property of the surface of the solid material is improved by reaction with them.

The surface to be modified can be, for example, an organic material, ceramic or a metal. Examples of suitable organic material comprise shaped objects made from a synthetic or natural polymer material. Thermo plastic or thermo settable resins, such as hydrocarbon resins and fluorinated hydrocarbons can be modified effectively according to the method of this invention. The solid material can have any desired shape, such as film, sheet, fiber, plate, block or rod.

The photoreaction which was triggered by irradiation with the UV laser beam is described in detail subsequently. If the solid layer which is made from a mixture which contains the photoreactive substance and the matrix material is irradiated with a laser beam, then the photoreactive substance disintegrates and forms reactive material types such as radicals, carbenes, nitrenes, etc. Since the matrix material is inert, the photo-disintegrated reactive material types are prevented from starting side reactions or chain reactions. Thus, the life time of the reactive material types is considerably long, such that the reactive material types can be retained in highly pure form in the matrix. Without such a matrix, the reactive material types collide with each other and reduce their purity. Therefore, it is important that the matrix material be contained in the solid layer.

Since a pulsed high-performance- laser beam is easily available, the photo-disintegration can take place similar to an explosion during the simultaneous production of reaction heat. The result is that the irradiated surface is immediately vaporized and ablated. The vaporized products (reactive material types and the inert matrix material) emitted in this way in a pulsed state due to ablation in the environment of inert matrix material have an advantage in the direction of emission. If the surface of a solid material is irradiated with the emitted, vaporized products, then the reactive material types which are obtained due to photo-disintegration and contained in the vaporized products react with the surface. By optimizing the

intensity of the laser beam and the type of photoreactive substance to be irradiated, it is possible to produce high reactive material types in high purity and high concentration suitable for modification of the surface of solid material.

As already described, the solid layer can have a multi layer structure in which two or more photoreactive substances are incorporated correspondingly in two or more stacked layers of the matrix material. By using two or more types of reactive materials in combination, high-reactive material types can be obtained. In such a case, two or more types of laser beams that are suitable for the current photoreactive substances are used for irradiation of the solid layer.

A modification of a solid material by treatment with reactive products takes place only on those surfaces that were irradiated with the reactive material types, such that the main quantity of desired properties of solid material is retained unchanged. The surface modification method according to the present invention can be used for improvement of different properties such as hydrophilicity, lipophilicity, adhesion capability, printability, non-linear optical characteristics, reflection property, refraction property, optical waveguide properties and cell deposition.

If desired, the irradiation of a surface of a solid material can be undertaken with the reactive material types by using a mask, such that a desired section of the surface can be selectively modified.

The following examples further illustrate this invention.

Example 1

A solid layer consists of perfluorohexane (matrix material) and pentafluorophenylazide (for photoreactive substance). Said layer was applied on a sapphire substrate which was placed in a vacuum vessel and cooled to 85 K. The molar ratio of the matrix material to that of the photoreactive substance was about 100:1. The solid layer was then irradiated with a KrF excimer laser with 25 mJ/cm^2/ pulse. It

was found that the solid layer was ablated. The luminescence spectrum showed that the vaporized products which were emitted by the solid layer contained perflurophenylnitrenes (Figure 1). A polyethylene terephthalate film was irradiated with a beam of vaporized products emitted by the solid layer. No change was observed with the naked eye. However, the photoelectron spectroscopic X-ray analysis showed that the irradiated surface contained C, N, O and F, while it had contained only C and O before irradiation (Figures 2 and 3). The above results show that the laser beam- irradiation produces perfluorophenylnitrenes which, in turn, is chemically bonded on the surface of a polyethylene terephthalate film. The contact angle of the surface of the polyethylene terephthalate film was changed from 70° to 110° as a result of irradiation with the beam obtained from vaporized products emitted by the solid layer. This shows that the hydrophobic property of the surface is improved.

Example 2

A solid layer consists of perfluorohexane (matrix material) and pentafluorophenylazide (for photoreactive substance). Said layer was applied on a sapphire substrate which was placed in a vacuum vessel and cooled to 85 K. The molar ratio of matrix material to that of photoreactive substance was about 100:1. The solid layer was then irradiated with a KrF excimer laser with 25 mJ/cm^2/ pulse. It was found that the solid layer was ablated. A monomolecular hexadecylthiol layer was applied on a gold substrate. This was irradiated with a beam obtained from vaporized products emitted by the solid layer. No change was observed with the naked eye. However, the photoelectron spectroscopic X-ray analysis showed that the irradiated surface contained S, C, N, and F while it had contained only S and C before irradiation. The reflection IR spectrum showed a peak (1525 cm^{-1}) which was ascribed to an aromatic ring. This appears to show that perfluorophenylnitrene is bonded on the irradiated surface whereby its aromatic ring is retained. The contact angle of the surface of the mono molecular hexadecylthiol layer

was changed from 90° to 130° as a result of irradiation with the beam obtained from the vaporized products emitted by the solid layer. This shows that the hydrophobic property of the surface is improved.

Example 3

A solid layer consisting of perfluorohexane (matrix material) and perfluoroacetic anhydride (for photoreactive substance) was applied on a sapphire substrate, which was placed in a vacuum vessel and cooled to 85 K. The molar ratio of matrix material to that of photoreactive substance was about 100:1. The solid layer was then irradiated with a KrF excimer laser with 25 mJ/cm^2/pulse. It was found that the solid layer was ablated. A monomolecular hexadecylthiol layer was applied on a gold substrate. This layer was irradiated with a beam obtained from vaporized products emitted by the solid layer. No change was observed with the naked eye. However, the photoelectron spectroscopic X-ray analysis showed that the irradiated surface contained S, C, N, and F while it had contained only S and C before irradiation. This appears to show that a trifluoromethyl group or a trifluoroacetyl group is bonded to the surface. The contact angle of the surface of mono molecular hexadecylthiol layer was changed from 70° to 120° as a result of irradiation with the beam obtained from the vaporized products emitted by the solid layer. This shows that the hydrophobic property of the surface is improved.

Example 4

A solid layer consists of perfluorohexane (matrix material) and hydrazine (for photoreactive substance). Said layer was applied on a sapphire substrate which was placed in a vacuum vessel and cooled to 85 K. The molar ratio of the matrix material to that of the photoreactive substance was about 100:1. The solid layer was then irradiated with a ArF excimer laser with 25 mJ/cm^2/ pulse. It was found that the solid layer was ablated. A polytetrafluoroethylene film was irradiated with a beam obtained

from vaporized products emitted by the solid layer. No change was observed with the naked eye. However, the photoelectron spectroscopic X-ray analysis showed that the irradiated surface contained C, N, and F while it had contained only F and C before irradiation. A reduction of F peak was also observed. The hydrophilicity of the surface was improved. This shows that a hydrophilic group (group containing N) is substituted for a part of F of the polyethylene terephthalate film.

Claims

1. Method for production of reactive material types, characterized in that a solid layer is obtained from a mixture of a matrix material with a photoreactive substance which is formed on a substrate; this layer is irradiated with a UV laser beam having a wavelength of 400 nm or shorter.

2. Method according to Claim 1, with which the UV laser beam is a ArF-excimer laser beam, KrF-excimer laser beam, XeCl excime laser beam or XeF excimer laser beam.

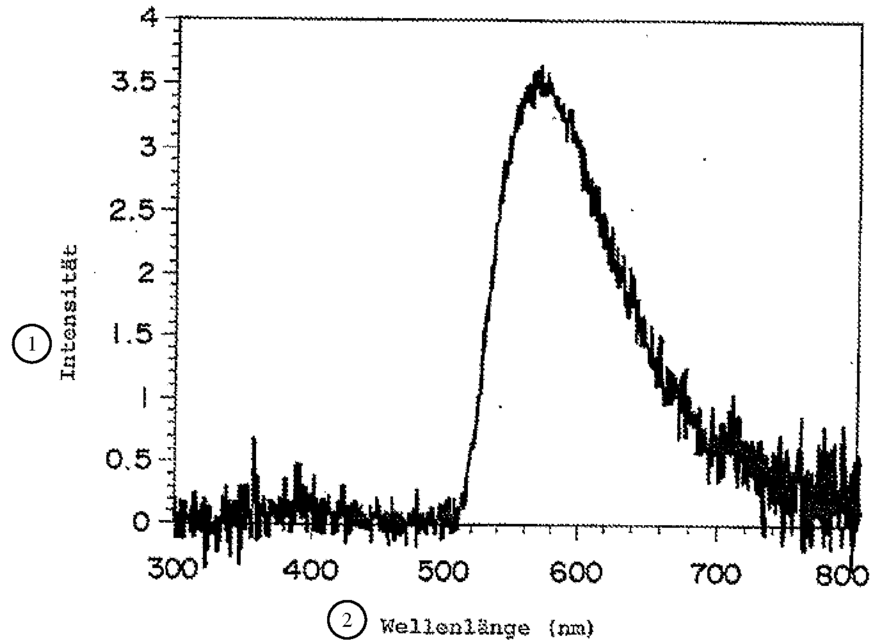
3. Method according to Claim 1, wherein the photoreactive substance is an azide compound, an azo compound, a carbonyl compound, an acid anhydride, a hydrazine or an organic halogen compound.

4. Method according to Claim 1, wherein the matrix material is a noble gas, a nitrogen gas, carbon dioxide, a fluorinated alkane, an alkane, an ether or an alcohol.

5. Method for modification of a surface of a solid material, characterized in that the surface is brought into contact with active material types which were produced according to a method according to Claim 1.

6. Method according to Claim 5, whereby the solid material is a polymer material.

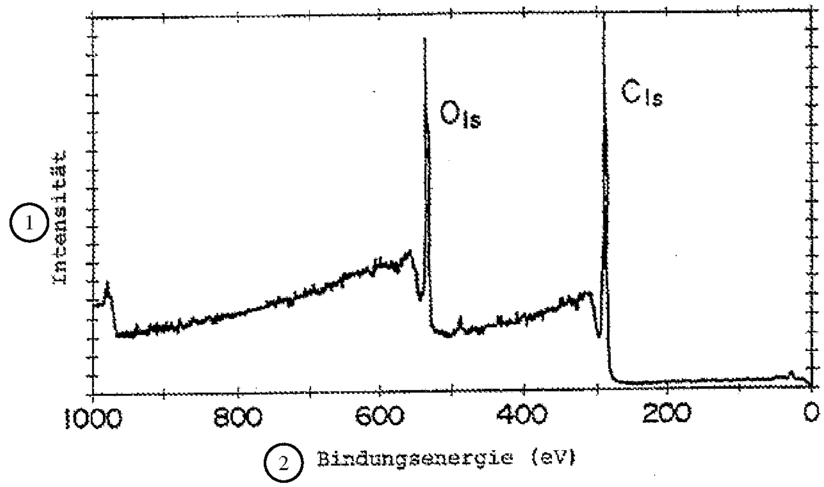
FIG. 1



Key: 1 Intensity

2 Wavelength

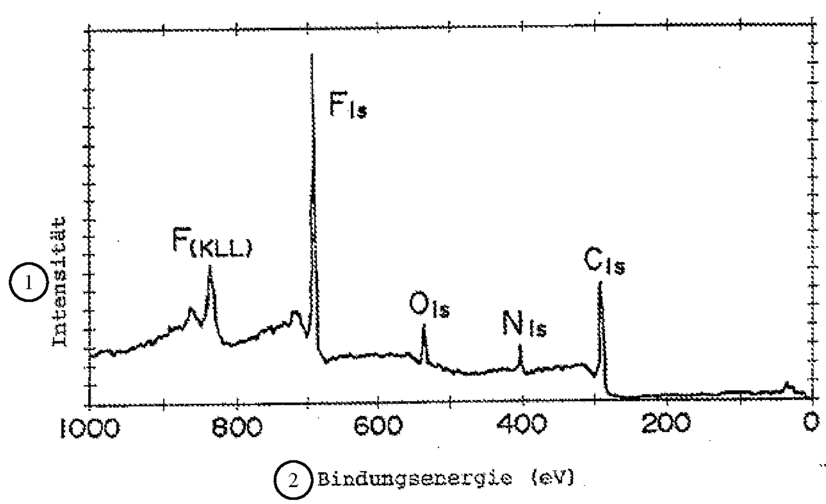
F I G. 2



Key: 1 Intensity

2 Bond energy

F I G. 3



Key:	1	Intensity
	2	Bond energy